Interface effects on H_2 adsorption and dissociation on gold clusters supported on the rutile $TiO_2(110)$ surface

(Kyoto University*, Hokkaido University**) ○Andrey Lyalin*, Min Gao**,
Satoshi Maeda*,**, Tetsuya Taketsugu*,**

Gold nanoparticles demonstrate their great potential as an effective catalyst for hydrogenation reactions. However, mechanisms of such catalytic reactions are largely not understood. In the present work we focus on the elucidation of mechanisms of H_2 activation and dissociation on the small free and supported gold clusters. It is demonstrated that adsorption of H_2 on gold clusters depends on cluster size, geometry structure, cluster flexibility and interaction with the support. In particular the role of the rutile $TiO_2(110)$ surface in the processes of H_2 adsorption and dissociation on the supported gold clusters is discussed.

We introduce a global reaction route mapping (GRRM) approach to find chemical bond activation pathways catalyzed by small free gold clusters Au_n (n=1–11) with the use of anharmonic downward distortion following (ADDF) and artificial force induced reaction (AFIR) methods [1-3]. The calculations have been performed as follows: (1) automated search for isomers of free gold clusters by ADDF method; (2) physical and chemical adsorption of H_2 on the obtained gold clusters by AIFR method; (3) refining the obtained AFIR paths to find transition states (TSs) for H-H bond dissociation. All calculations are carried out using density-functional theory (DFT) with the PBE gradient-corrected exchange–correlation functional [4]. The results of our calculations demonstrate that H_2 molecule prefers to bind to the low-coordinated gold atoms on the most stable cluster isomer. However, in that case the barrier for H_2 dissociation can be relatively high. On the other hand in GRRM approach both the global minimum (GM) and several local minima (LM) are considered simultaneously on the basis of ADDF and AFIR methods. Such approach allows one to reduce considerably the barriers for H_2 dissociation, as it is shown in Figure 1.
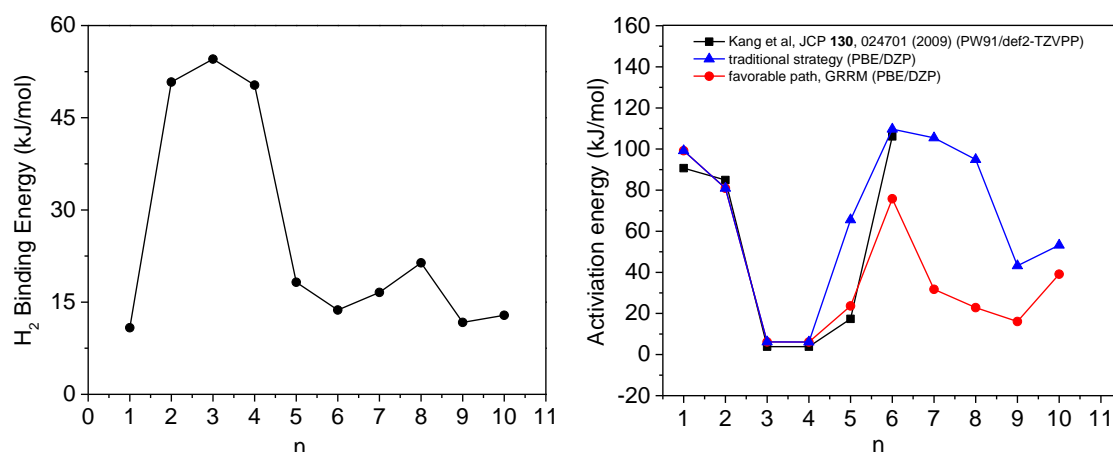

Figure 1. Binding energy of H_2 adsorbed on Au_n clusters as a function of cluster size (left); activation energy for H_2 dissociation obtained with the use of the traditional strategy (triangles) and GRRM approach (dots) as a function of cluster size (right).

It is well known that the support material can play an important role in the catalytic processes, considerably influencing the chemical reactivity of the supported clusters [5]. Thus, recently it was demonstrated experimentally that the perimeter interface between the cluster and the support material can play the role of active sites for hydrogen dissociation by gold nanoparticles on TiO_2 support [6]. Therefore we have performed theoretical calculations of adsorption and dissociation of H_2 molecule on the gold clusters supported on the rutile $TiO_2(110)$ surface [7]. We have demonstrated that TiO_2 (110) support considerably affects geometry structure of the supported gold clusters and promotes adsorption and dissociation of H_2 on Au_n/TiO_2. In particular, formation of the OH group near the supported gold cluster is an important condition for H_2 dissociation, as it is shown in Figure 2. The active sites for H_2 dissociation are located in the vicinity of the low coordinated oxygen atoms on the rutile $TiO_2(110)$ surface [7]. This, combination (interplay) of several factors such as geometry structure, cluster dimensionality, presence of the low coordinated oxygen atoms in the vicinity of the cluster-surface interface, etc. are important for H_2 dissociation.
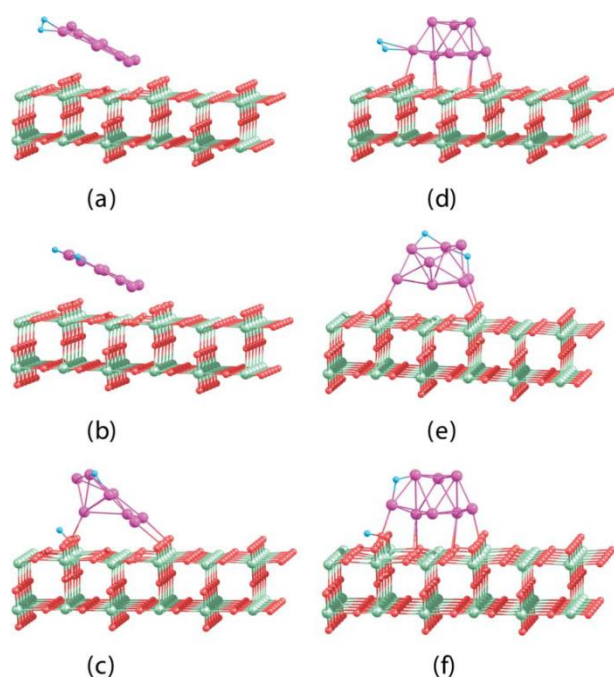

Figure 2. Optimized geometries in the case of (a) molecular adsorption of H_2 on $Au_8(2D)/TiO_2$, E_b = 23 kJ/mol; dissociative adsorption of H_2 on $Au_2(2D)/TiO_2$: (b) dissociation of H_2 on supported $Au_2(2D)$, $E_b = 72$ kJ/mol; (c) dissociation of H_2 with formation of the OH group on O(2) bridge atom, $E_b = 150$ kJ/mol. Optimized geometries in the case of (d) molecular adsorption of H_2 on $Au_8(3D)/TiO_2$, $E_b = 9$ kJ/mol; dissociative adsorption of H_2 on $Au_2(3D)/TiO_2$: (e) dissociation of H_2 on supported $Au_2(3D)$, $E_b = 53$ kJ/mol; (f) dissociation of H_2 with formation of the OH group on O(2) bridge atom, $E_b = 92$ kJ/mol.

References
[1] K. Ohno and S. Maeda, *Chem. Phys. Lett.* **384**, 277 (2004).
[2] S. Maeda and K. Morokuma, *J. Chem. Phys.* **132**, 241102 (2010).
[3] S. Maeda, K. Ohno, and K. Morokuma, *Phys. Chem. Chem. Phys.* **15**, 3683 (2013).
[4] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 77, 3865 (1996).
[5] M. Gao, A. Lyalin, and T. Taketsugu, *J. Chem. Phys.* **138**, 034701 (2013).
[6] T. Fujitani, I. Nakamura, T. Akita, M. Okumura, and M. Haruta *Angew. Chem. Int. Ed.* **48**, 9515 (2009).
[7] A. Lyalin and T. Taketsugu, *Faraday Discuss.* **152**, 185 (2011).